Mineral Sciences
Division
A.T. Prince, Chief.

555 Booth Street,
Ottawa 4, Ontario,
November 15, 1965.

Dr. Allan C. Turnock,
Department of Geology,
University of Manitoba,
Winnipeg, Manitoba.

Dear Allan:

Many thanks for your letter of October 28th, enclosing a suggested revised manuscript for the note on "Non-Stoichiometric Tantalian Magnetites". Using this as a basis, and also incorporating parts of the earlier version, together with comments by John Rowland and Ernie Nickel, we eventually came up with the enclosed final version, of which two copies are herewith sent to you for your retention.

I have had three copies reproduced on one side of the page only and am today sending them in to Frank Reed, the Editor of the "Journal of the American Ceramic Society", with the request that the document be considered for publication in the "Note" series in the Journal.

Insofar as the Mn-Ta-O paper is concerned, this has been typed, approved all the way up the line, approved for publication and is at present away at the Queen's Printer. When it is returned, I will get three copies reproduced on one side of the page only for publication purposes. I will send these three copies, along with several normal copies for your retention, and also glossy prints of the one figure involved, all to you, in order that you may submit them to the Editor of the journal yourself at your convenience.

I am glad to hear that things are going well with you and that the outlook with the baby's health is more optimistic. The weather here, for November, has really not been too bad, when one takes into account my view that winter is a useless business anyway.

Our Japanese Post-doctorate Fellow arrived last month and is now well settled in, has set up his equipment and is happily engaged in investigating some problems connected with the Ti-O system that I encountered some years ago and never had the opportunity to work out

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to completion.

I've been in some demand as a speaker recently, having spoken to the C.I.C., McGill University Chapter, and also to the staff of the Noranda Research Centre at Pointe Claire, Quebec.

I will write to you again when the copies of the Mn-Ta-O paper become available. Meanwhile, all the very best to you and yours.

Yours very sincerely,

N.F.H. Bright,
Head,
Physical Chemistry Section.

Enclosures.

Dr. N.F.H. Bright

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CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS

MINES BRANCH

OTTAWA

MINERAL SCIENCES DIVISION

INTERNAL REPORT MS-65-99

NON-STOICHIOMETRIC TANTALIAN MAGNETITES

by

Norman F.H. Bright and Allan C. Turnock

Note prepared for publication in the
"Journal of the American Ceramic Society"

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September 13, 1965

MINES BRANCH

Mineral Sciences Division

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(Author)s Norman F.H. Bright
Allan C. Turnock

(Date) Sept. 13, 1965.

Internal Investigation Report No. MS-65-99

TITLE:

NON-STOICHIOMETRIC TANTALIAN MAGNETITES

(25 cc.)

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8	" " " " "		
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A.T. Prince

Mineral Sciences Division Internal Report MS-65-99

NON-STOICHIOMETRIC TANTALIAN MAGNETITES

by

Norman F.H. Bright* and Allan C. Turnock**

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In two recent publications[1,2] it has been demonstrated that tantalum and niobium can be introduced into the magnetite, Fe_3O_4, spinel lattice by the substitution:

$$3\ Fe_3O_4 \longleftrightarrow Fe_7^{2+}(Nb \text{ or } Ta)_2^{5+}O_{12}$$

The spinel structure is maintained at the temperatures investigated, up to about 80% substitution of the Fe^{3+}. These substituted compounds retain the 3:4 cation:anion ratio of stoichiometric spinels. In the case of the tantalian spinels[1], it was further shown that non-stoichiometric spinels, in which this ratio departed significantly from the 3:4 value, could readily be obtained, whereas, in the case of the niobian spinels[2], very little departure only from the 3:4 stoichiometry was tolerated. This non-stoichiometry was referred to as being of the cation-excess type.

On the basis of the experiments reported, however, the non-

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stoichiometry could have been caused by either (a) excess cations present interstitially in an essentially undisturbed anion (oxygen) lattice, (b) vacancies in the oxygen lattice, with an essentially undisturbed arrangement of cations or (c) extra metal ions occupying oxygen sites, leaving the interstice structure of the lattice essentially undisturbed. The arithmetic stoichiometry of all three types would be equivalent. A decision as to which type of non-stoichiometry is actually occurring can be arrived at by a consideration of the densities and cell-edges of the non-stoichiometric spinels when compared with those of stoichiometric spinels of the same Fe:Ta ratio. The sizes of the various ions involved in these compounds are as follows: Fe^{2+} = 0.83, Fe^{3+} = 0.67, Ta^{5+} = 0.68 and O^{2-} = 1.32 Angstrom units. Case (a), above, would produce an <u>increase</u> in density and, possibly, a smaller proportionate <u>increase</u> in cell edge. The dilatation of the lattice would probably not be great since the spinel oxygen framework contains many holes of a size adequate to accommodate extra cations with little difficulty. Case (b) would produce a <u>decrease</u> in density with, possibly, a smaller <u>decrease</u> in unit cell volume, whereas Case (c) would produce a significant <u>increase</u> in density, probably accompanied by a <u>decrease</u> in cell size since the metal ions are substantially smaller than the oxygen ions they replace.

In order to resolve this problem, therefore, it was necessary to conduct density measurements and to consider also the previously-determined cell edges. Accordingly, density measurements were made on two pairs of samples of tantalian magnetites having differing Fe:Ta atomic ratios, one

member of each pair being stoichiometric in cation:anion ratio and the other being non-stoichiometric. The measurements were made using a two-millilitre pycnometer with pure toluene as the immersion liquid. Owing to the smallness of the available samples, only one determination on each material could be made and the accuracy of the results is, therefore, not readily predictable. The results obtained are given in Table I.

TABLE I

Compositions and Density of Tantalian Magnetite Spinels

(N.B: N = non-stoichiometric; S = stoichiometric)

Sample Number	Fe:Ta Atomic Ratio	Composition (at.%)			Stoichiometry (S or N)	Unit Cell Edge (A)	Density (g/cm^3)
		Fe	Ta	O			
FT10-1	6:1	36.74	6.12	57.14	S	8.565	5.8_5
FT10-2	6:1	37.71	6.29	56.00	N	8.625	6.0_1
FT8-3	9:1	38.58	4.28	57.14	S	8.510	5.4_7
FT8-4	9:1	40.77	4.53	54.70	N	8.625	5.5_0

The non-stoichiometry was achieved by exposure of the stoichiometric spinels to an atmosphere sufficiently reducing that oxygen was lost from the sample. The extent of the loss was determined from the weight of the sample, oxygen being the only volatile species present at the temperature used, 1200°C. From the oxygen content and the known starting Fe:Ta ratios, the at.% compositions were readily computed.

These samples are, respectively, those referred to as Nos. 3, 5, 2 and 4 in Table III of the earlier work[1]. It will be observed from the above Table that the introduction of non-stoichiometry into the spinel is accompanied by an increase in both density and unit-cell edge. This is consistent with Case (a), viz., that the excess cations enter the lattice interstitially, leaving the oxygen framework essentially undisturbed though slightly dilated. This being so, the question remains as to whether both types of metal ion (iron and tantalum) are being accommodated or whether the excess cations are all of one type. This could only be determined with certainty from a detailed analysis of the atom positions in a full X-ray crystallographic study.

If, in replacing the Fe^{3+} ions by Ta^{5+} and Fe^{2+} ions according to the equation: $3\ Fe^{3+} \longleftrightarrow Ta^{5+} + 2\ Fe^{2+}$, which is the type of replacement that is suspected to occur, only one type of excess cation enters the spinel lattice, then it is probable that a second phase, in addition to the spinel, would appear in order to accommodate the other type of excess cation. Even with the more heavily substituted non-stoichiometric spinels, no such second phase was observed by X-ray diffraction of the products. This is considered to support the view that both types of excess cation are accommodated.

On the basis of these considerations one can compare the observed and calculated densities for the non-stoichiometric spinels. Taking the unti cell edge for stoichiometric magnetite, Fe_3O_4, to be 8.395 A.U, plotting the best straight line through this point and the observed

cell edges for the stoichiometric substituted spinels, and extrapolating to the theoretical limit of substitution of Fe^{3+} in Fe_3O_4 by (Ta^{5+} + 2 Fe^{2+}), viz., $Fe_7^{2+}\ Ta_2^{5+}\ O_{12}^{2-}$, one obtains a value of 8.65_6 Angstrom units as the cell-edge for this theoretical compound. One can then readily calculate the density of this theoretical end-member and obtain a figure of 6.454 g/cm^3. The density of pure magnetite is 5.201 g/cm^3. If the substitution of tantalum into magnetite produces an incease of density that is linear with the tantalum content, it will be seen that all the four density figures quoted in the above table lie below the theoretical straight line, although they are consistent in relative position. This is attributed to the experimental difficulty of getting good density measurements on very small quantities of fine powders. Such difficulties tend to give low figures.

On the basis of 8 molecules per unit cell, which is normal for spinels, and on the assumption that each molecule contains exactly 4.000 oxygen ions, then the number of excess iron and tantalum ions per unit cell in the two non-stoichiometric spinels quoted in the above table can be calculated to be as follows:

Spinel	Excess Iron	Excess Tantalum
Fe:Ta = 6:1	0.976	0.163
Fe:Ta = 9:1	2.248	0.249

These figures are based on the compositions given in Table I and are, thus, experimental values. This means that, in one case, about 1 extra ion has to be accommodated in the unit cell and in the other, about 2.5 ions. There is adequate space available to permit this accommodation and it is considered

probable that the excess ions are randomly distributed over available interstices. Any ordering of distribution would lead to the development of superlattice lines in the X-ray patterns; none such was observed. Neither the tantalian nor the niobian magnetites appeared to be able to tolerate the reverse non-stoichiometry to any detectable extent, viz., cation deficiency or anion excess.

The degree of non-stoichiometry observed with the niobian magnetites was too small to enable density measurements and cell-edge determinations to distinguish between cation-excess or anion deficiency, within the experimental limits obtaining in this investigation. It is thought probable, in view of the similarity in ion size of Nb^{5+} (0.69 A.U), that a similar situation as that for tantalum will exist. No explanation can be offered, however, for the marked difference in the extent of non-stoichiometry tolerated by tantalian magnetites compared with that tolerated by niobian magnetites.

ACKNOWLEDGEMENTS

The authors wish to express their thanks to their colleagues Dr. E.H. Nickel and Mr. J.F. Rowland, for useful discussions of this problem, and to Mr. D'Alton R. Owens for the density determinations.

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2. A.C. Turnock, "Fe-Nb Oxides: Phase Relationships at 1180°C", J. Am. Ceram. Soc., in press.